A view of water quality from the Plynlimon watershed

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Abstract

A summary of hydrochemical research in the Plynlimon catchments from 1983 to the present is related to identifying water flow pathways within catchments and the modelling of soil and stream water acidification. The study reveals a highly heterogeneous system that barely conforms with current understanding of hydrology and acidification theory. The role of hydrochemical mixing processes and groundwater flow routing is emphasised as is the need for maintaining long term monitoring studies and enhancing process based studies of water and chemical fluxes through catchments. The applicability of current environmental impact models for predictive and environmental management purposes is questioned and it is proposed that new hydrochemical modelling structures are needed to examine the highly heterogeneous systems being modelled.

Introduction

The Plynlimon catchments have been the focus of extensive and intensive environmental field studies for over 30 years (McCulloch, 1997; Neal, 1997; Hudson *et al.*, 1997a,b). Although the studies originally centred on hydrology, the major growth in research in the mid 1980s was in water quality studies (Reynolds *et al.*, 1986, 1989a, 1997) (Neal *et al.*, 1990a, 1997a,b). This growth (Neal, 1997 and Fig. 1) reflects the major environmental concerns of the 1970s and 1980s, atmospheric deposition of acidic oxides (so called 'acid rain') and the effect of forestry practices on stream water quality with subsequent deterioration in stream ecology (UKAWRG, 1988; Mason, 1990; Edwards *et al.*, 1992).

Papers contained in this volume of HESS and earlier work summarised of Kirby *et al.* (1991) provide an assessment of the broad findings of the Plynlimon study. In this final chapter, the water quality issues addressed over the past 14 years at Plynlimon are examined. This overview of water quality research indicates areas of past success in water quality studies and associated modelling endeavours and provides a personal statement of contemporary and future research needs at Plynlimon within the context of a decreasing enthusiasm for catchment research and a growing emphasis on computer simulation models to describe both short and long term environmental impacts. The paper demonstrates the importance of (a) continued monitoring of long term chemical changes in association with all the relevant hydrological variables, (b) strong linkages between observation and modelling and (c) scientific objectivity and model testing, the need for which remains as strong today as it was at the time of inception of the Plynlimon study.

Acidification and Environmental Impacts

From the late 1960s, concerns were raised over acidic deposition of industrially emitted acidic oxides (SO_x in particular) adversely affecting stream and lake ecology across Europe. The environmentally acid sensitive areas possessed acidic soils. The main features associated with the soil and stream water acidification occurs mainly because of the inability of weathering reactions of primary rock minerals to release base cations and neutralise acidic inputs. Following heated political debate, scientific research was undertaken to characterise the nature of the acidification process and to identify potential remedial treatments. The research at Plynlimon became an integral part of a major United Kingdom-Scandinavian research initiative, the Surface Water Acidification Programme (SWAP; Mason, 1990).

For the United Kingdom, considerable evidence has accumulated showing that acidification of the uplands has occurred. What is not often realized is the extent to which humans have influenced the water quality and ecology of the British upland environments. Indeed, very little of the British environment for either upland or lowland areas can be classed as being 'natural' or in an equilibrium state (Ingrouille, 1995). For example, the first phase of soil acidification probably started several to ten thousand years ago with the development and subsequent loss of birch, hazel, alder and oak forests due to both climate change and man's

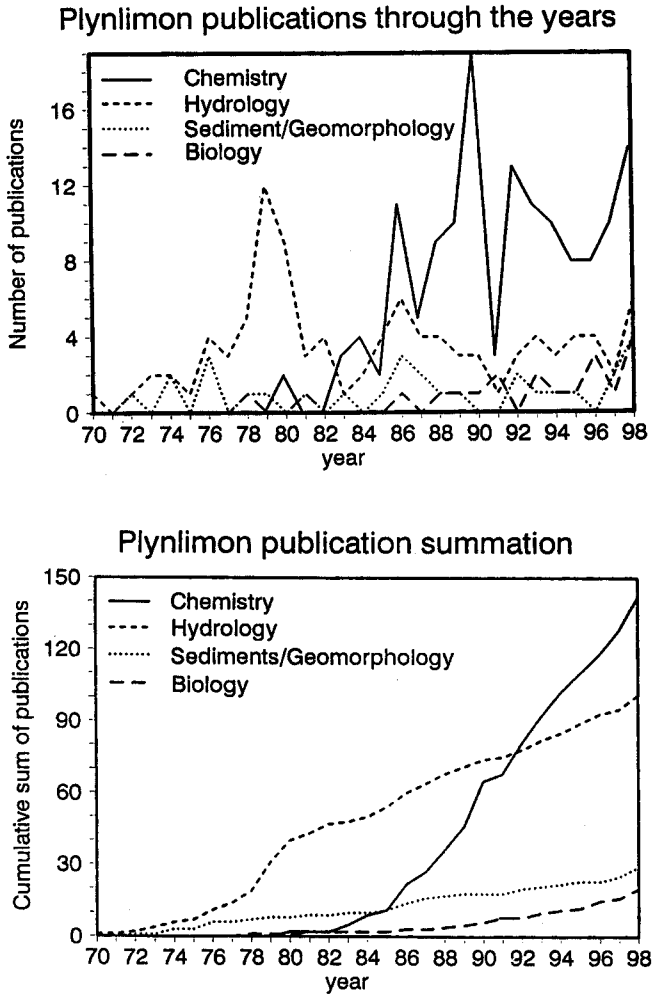

Figure 1. *Graphs showing the publication record for the Plynlimon study over time for the main study disciplines of Hydrology, chemistry, biology and sedimentology/geomorphology.*

impact on the environment (Neal *et al.*, 1997b). Hence, thin acidic moorland soils developed and these are characteristic of much of the British uplands today. During the past hundred years, a further ecologically potent phase of acidification has occured which is associated with acidic oxide deposition and, to a much lesser extent, conifer planting: the driving force is the former, while conifers enhance the capture of acid pollutants, thereby increasing their impacts. While acidification of the soils occurs by 'natural processes', it is the added constraint of changing atmospheric inputs and/or land disturbance that can lead to major changes in the stream.

The Plynlimon hydrochemical experiment

FOUNDATIONS TO THE RESEARCH

In the spring of 1983, the Plynlimon hydrological research programme was extended to characterise the effects of forestry management on stream water quality. The underlying approach was to study a wide range of chemical constituents to assess (a) hydrological flow pathways at the catchment level and (b) the impacts of conifer harvesting (Neal *et al.*, 1990a). Initially, the Hafren and the Hore, two main sub-catchments of the headwaters of the River Severn in the Hafren forest, were selected but monitoring was extended later to encompass moorland and forested sub-catchments, ephemeral streams and groundwater zones (Neal *et al.*, 1997a,c; Hill and Neal, 1997) as well as stemflow and throughfall for the forest canopy and occult inputs from mist (Neal *et al.*, 1992a, 1997a; Wilkinson *et al.*, 1997).

BASIC WATER QUALITY FINDINGS

Plynlimon rainfall is derived from a variety of sources; its chemical composition reflects both sea-salts (air masses from the Atlantic Ocean) and pollutant inputs (air that has passed over agricultural land and industrial areas). Due to the changing meterological conditions, the chemical composition varies substantially (Neal *et al.*, 1990a, 1992a; Wilkinson *et al.*, 1997). Rainfall does not usually pass directly through the catchment to provide the major volume of water in the stream. This is shown by the marked contrast between rainfall and stream water chemistry for chloride, a chemically conservative element. Thus, while chloride shows high variability within the rainfall, the chemical signal in the stream is almost completely damped out (Neal *et al.*, 1997a). In spite of this, large fluctuations in many chemical species occur in the stream because of hydrological variations. Baseflow waters have higher calcium and silicon concentrations and alkalinities than the corresponding stormflow waters which have higher concentrations of aluminium, several trace metals and hydrogen ions. This difference reflects the large chemical gradients within the catchment: the soil zones are organic and aluminium oxide/hydroxide rich and they produce acidic, aluminium- and transition metal- enriched soil water; the bedrock has weatherable and acid-soluble inorganic components with the capacity to neutralise these acid waters and precipitate the easily hydrolysable transition metals and aluminium (Neal *et al.*, 1990a, 1997a–c).

Under conditions of baseflow, water drains mainly from near the stream bank and from the groundwater areas while a far greater proportion of streamflow water comes from the soil (Neal *et al.*, 1990a,b). Variations in the bedrock composition lead to differences in the stream water chemistries of the Afon Hafren and Afon Hore. For example, the presence of calcite and lead and zinc sulphides in the Hore catchment leads to higher calcium concentrations and measurable lead and zinc concentrations in the streams (Reynolds *et al.*, 1986; Neal *et al.*, 1990a).

Superimposed on this behaviour are two other patterns. Firstly, seasonal patterns are observed. These relate to the nutrients such as nitrate, boron, bromide and iodine,

whose concentrations are to a large degree linked to the biological functioning of the catchment (Neal *et al.*, 1997a). However, the patterns are not always very regular. For example, there may be occasional extended dry periods or periods of temperature extreme where the catchment is perturbed to release nitrate and sulphate (Durand *et al.*, 1994; Neal *et al.*, 1997a). Secondly, there are longer term patterns of ten years or more (decadal) for components such as the sea-salts, sulphate and certain heavy metals that are probably linked to changing atmospheric loadings as influenced by changing weather patterns (Robson and Neal, 1996; Neal *et al.*, 1997a).

With deforestation, uptake of nutrients into the growing biomass is reduced initially. This, coupled with enhanced decomposition processes leads to releases of nutrients to the stream for up to five years: after that time nutrient concentrations return to pre-felling levels (Neal *et al.*, 1992a–c; Reynolds *et al.*, 1995). Smaller effects are observed for the inorganic components which relate to catchment acidification: for the first few years after felling calcium and alkalinity concentrations decline particularly during the summer, when the baseflow contributions are at their highest. This implies that it is the groundwater which shows the major signs of acidification.

Splitting the chemical hydrograph

THE RELATIVE CONTRIBUTIONS OF SOIL WATER AND GROUNDWATER TO STREAM-FLOW GENERATION

The flow-related variations in stream water chemistry are linked, at a gross scale, to varying contributions from soil and ground water inputs to determine the dynamics of stream water supply. Most chemical components which respond to flow are chemically reactive; hence conservative mixing formulations cannot be used. To assess stream water mixing relationships, the concentration changes for the most variable but chemically conservative tracer, acid neutralisation capacity (ANC), have been used to split the hydrograph into soil and groundwater 'endmember' components (Neal *et al.*, 1990b; Robson *et al.*, 1990; Christophersen *et al.*, 1990; Robson, 1993). Baseflow is assumed to be representative of the groundwater chemistry and average baseflow ANCs have been used to depict the endmember value. Within the soil zones, mean ANC differs for the grassland and forested parts of the catchment and arealy averaged values have been used for the calculations. As flow increases, the proportional contribution of soil water from the hillslope increases and then levels off at high flows. At baseflow, the majority of the water (>90%) comes from groundwater sources. However, even under high flow conditions, the groundwater component can contribute (>20%) to the total flow (Neal *et al.*, 1990a,b; Robson, 1993).

DETERMINING SOIL AND GROUNDWATER END-MEMBER COMPOSITION VARIATION

Up to about five years ago, the only measurement of soil water chemistry was based on samples taken using tension and plate lysimeters and these results showed a very high variability. Given (1) the large variability in lysimeter water chemistry data observed both at Plynlimon and elsewhere (Robson, 1993; Taugbøl and Neal, 1993), (2) the high variability implied in soil pore waters based on measurements of exchangeable cations (Neal, 1996; Neal and Robson, 1997) and (3) the time consuming nature of sampling waters using tension and plate lysimeters, it was decided to measure the soil endmembers using runoff from small streams where soil drainage might be expected to be high (Neal *et al.*, 1997c; Hill and Neal, 1997).

For groundwaters, no measurements were taken until the early results of the hydrograph splitting approach indicated groundwater in the area. In consequence, an extensive set of boreholes was introduced within the catchment to prove the widespread occurrence of shallow groundwater in the area (Neal *et al.*, 1997d,e).

The results of the enhanced sampling programme showed a large spatial and temporal variation in chemistry for both soil and groundwater. The soil waters were mainly more acidic than their groundwater counterparts and their acidity changed as a function of flow with alkalinities usually being highest under low flow conditions. Thus, it seems that even the near surface runoff is determined, in part, by groundwater supplies and the amount of the groundwater contribution varies in an erratic way across the catchment. In general, the alkalinity was higher in the groundwater than in the soils but there was considerable overlap from site to site. During wet periods, groundwater alkalinity was often at its lowest; this indicates that the chemistry of the groundwater is, in part, controlled by soil water inputs. One very surprising feature of the introduction of a borehole near one of the streams was that it changed the hydrological pathways and the character of the stream by increasing the alkalinity and base cations supplied by weathering (Neal *et al.*, 1997e).

Thus, neither soil- nor ground- waters occur with fixed chemistry. Indeed, as one examines the catchment in finer detail (e.g. using soil lysimeters), the nature of the catchment becomes more heterogeneous with respect to endmember compositions. Rather than having endmembers as such, there is a gradation in chemistry determined at different sites for both soil- and ground- water mixing erratically as a function of chemical weathering rate and water transit routing.

APPLYING CHEMICAL MIXING TECHNIQUES WITHIN A MODELLING CONTEXT

Throughout the hydrochemical studies at Plynlimon, parallel modelling initiatives have been taken to explore short-term (event) and long-term (decadal) changes in

chemistry. With regards to hydrochemical mixing models, two short term event approaches (the Birkenes model and TOPMODEL) and one long term modelling approach (MAGIC) have been used for studies at Plynlimon. The results are described below.

Birkenes model

The Birkenes model comprises two reservoirs which represent soil and groundwater areas (Christophersen *et al.*, 1982, 1984). Within these reservoirs, simple equations represent hydrological rainfall-runoff processes and chemical reactions that relate to equations from the classic soil science literature. Within the soil reservoir, chemical reactions involve mainly cation exchange while in the groundwater reservoir, chemical weathering predominates: in both reservoirs physical mixing processes also occur. The Birkenes model was used to examine two contrasting chemical signals (Neal *et al.*, 1988):

1) alkalinity. This varies systematically with flow and is associated with 'internal' catchment chemical processes;
2) chloride. This is derived from the atmosphere. It is chemically unreactive in the catchment and shows a damped response in the stream.

The model was first calibrated for hydrology using a one year data record. The results showed an extremely good fit. Indeed, early simulations identified short periods when the hydrological record was incorrect. The model represented both hydrogen ion concentrations and alkalinity well. However, when the model was run for chloride, serious discrepancies occurred and the model could not mimic the high damping of the rainfall signal and the flow related hydrogen ion and alkalinity signals observed in the stream simultaneously.

During the analysis, it was realized that the depiction of catchments in terms of upper and lower reservoirs was incorrect; the Plynlimon catchment is long (one kilometre) while the soil depth is small (usually less than one metre) so that water, on travelling through the various soil layers in the catchment to the stream, has many opportunities to mix by stochastic flow routing processes and, hence, to produce the required damped chloride response. The much better fit for alkalinity/pH is explained by (a) the very similar nature of the rainfall and runoff signals and (b) the strong correlation between flow and alkalinity/pH.

The poor modelling fits for chloride indicate not only the heterogeneous flow routing and weathering observed in the field as described earlier in this presentation but also the value of this unreactive anion as a chemical tracer. Further, despite the elegance and simplicity of the Birkenes model, extra processes needed to be included to match prediction and field observation. These have yet to be found conclusively from field evidence (Lundquist *et al.*, 1990).

TOPMODEL

Chemical modelling was undertaken using a more distributed approach to that of the Birkenes model (TOPMODEL: Beven and Kirkby, 1979; Beven *et al.*, 1984). TOPMODEL represents evapotranspiration, interception, and transpiration losses coupled with estimates of saturated sub-surface flows, unsaturated flow and quick flow. The essence of TOPMODEL's hydrological structure lies in an exponential transmissivity curve which determines the saturated flow characteristics. Catchment topography is examined by means of a topographic index determined from a digital terrain map across a grid covering the catchment. The modelling study for Plynlimon examined the link between the hydrological and the chemical response of the stream on an episodic basis using continuous measurements of pH and conductivity as well as weekly signals for chloride (Robson, 1993; Robson *et al.*, 1992a,b, 1993). TOPMODEL was adapted so that the contributions to the stream from different soil horizons could be estimated from different soil layers within the catchment.

The model structure was capable of explaining stream chemistry assuming mixing relationships to be appropriate. However, at least four endmembers were required to model the data and the parameters were not particularly well defined: cross validation did not produce very good results (Robson, 1993). Examination of the continuous chemical measures indicated that there were significant chemical stores with which rainwater could mix in the soil zones. The results mimic those of the Birkenes case: the stores account for the high damping of the rainfall inputs with regards to chloride (and conductivity) although data fits are better for alkalinity due to the correspondence of alkalinity change with flow. The modelling results indicate a wide range of residence times for rainwater: the oldest stores of water, seen mainly at baseflow, change composition only very slowly. The upper soil waters change more rapidly, but are still highly damped relative to rainfall: it seems that only 2/3 of the rainfall input leaves the catchment within three months of the rainfall event.

The results indicate that water within the catchment cannot be treated as having a uniform chemistry; again, this fits well with the heterogeneous nature of the catchments observed in the field.

MAGIC

The model MAGIC (Modelling Acidification of Groundwater In Catchments: Cosby *et al.*, 1985a,b) has been widely used within acidification research for predicting yearly to decadal and longer changes in stream water chemistry in relation to changing atmospheric pollution loadings. It represents catchments in terms of an atmospheric input which can be varied over time, a soil compartment where a series of cation exchange, weathering, inorganic carbon, sulphate adsorption and aluminium hydroxide solubility controls operate and a stream output where carbon dioxide degassing and aluminium hydroxide

solubility controls modify the chemistry of the soil water entering the stream. For the application of the MAGIC model to the Plynlimon catchments, a more elaborate scheme has been used whereby the soil compartment is split between a soil zone and a groundwater zone where cation exchange and weathering reactions predominate respectively. This model has been applied to the moorland Afon Gwy catchment of the Plynlimon system by defining the soil and groundwater endmember compositions and the relative proportions of water passing between these two stores based on the hydrograph splitting techniques described above and a two component non-conservative mixing process for inorganic aluminium (Neal *et al.*, 1992e, 1997b—see also the discussion later in the paper). The results provide (a) a long term assessment of how the average stream, soil and groundwater chemistries change from year to year with changing atmospheric pollution levels and (b) the distribution and frequency of acidification events linked to hydrological variations (Robson *et al.*, 1991; Forti *et al.*, 1996; Neal *et al.*, 1992e, 1997b). While continuous measurements can be used to test the Birkenes model and TOPMODEL, this technique cannot be used to test the MAGIC model as a much longer time frame is involved. Later in this paper, the assumptions of the chemical basis for the reactions will be examined.

CHEMICAL PROCESSES WITHIN A COMPLEX HETEROGENEOUS ENDMEMBER CONTEXT

The results presented above demonstrate the variability of soil and groundwater chemistry and the problems of interpreting chemical signals within simple hydrological formulations. However, in relation to acidification patterns, it is not simply the linkage between chemistry and hydrology that matters but also how the soil and groundwater compositions change with time in relation to changes in atmospheric pollution deposition or climate.

To understand the complex and variable nature of environmental systems, it is necessary to average data in a way that simplifies and mimics the broader features of environmental response. In the case of heterogeneous soil and groundwaters, this simplifies to the question of how average compositions vary. Unfortunately, there is a inconsistency: most of the chemical reactions involved in the acidification process are non-linear so that average(F(x)) seldom equals F(average(x)) (Neal, 1992). This problem has been almost universally ignored by the environmental research fraternity.

It is not just surface runoff which shows large spatial and temporal variation. Soils also vary in relation to physical make up and in their chemical and hydrological properties (Neal, 1992, 1996; Taugbøl and Neal, 1993). However, hydrochemical models of catchments have, by their nature, 'lumped' such variability so that the model structure remains manageable. This means that the soils and soil-waters are assumed to have a homogeneous composition. For catchment-based hydrochemical models, it is essential to establish how the soil variability influences the stream chemistry because water draining from the soil provides a chemically and hydrologically important component of storm runoff.

To tackle this issue, several computer-based studies have been undertaken. These studies use synthetically generated data to examine how heterogeneity affects the properties of averaged quantities (Neal, 1992, 1996; Neal and Robson, 1994, 1997). The results indicate a large spatial variation in local soil-micropore water chemistry. However, the relationships between averaged cation and anion concentrations modelled compare reasonably well with what would be expected from a homogeneous system representative of averaged conditions. This indicates, at first sight, that the properties of the averaged data may be represented by homogeneous cation exchange—provided the equilibrium constants for cation exchange do not vary considerably within the soil (Neal and Robson, 1997).

While this may be the case for computer-based desk studies, the real test for chemical equilibrium rests with field measurements. Consequently, the cation exchange reactions were examined for a small stream (south-2-Hore) draining into the Hore catchment at Plynlimon where large variations in stream chemistry occurred but where surface runoff would be expected to drain essentially the soil zone (Neal *et al.*, 1994). The computer-based simulations indicate that stream runoff chemistry for soil waters should obey simple patterns of behaviour. In particular, the relationships between cation concentrations with changing anion concentrations should follow simple power relationships: for ions M and N of charges m+ and n+ respectively, the concentration of M should be proportional to the concentration of N raised to the power m/n (Neal, 1996). The data when examined in this light do not conform with cation exchange theory. Thus, the power relationships observed between cations differ from those given by theory for homogeneous cation exchange. Indeed, power relationships describing their co-variations, at least for the monovalent and divalent cations, lie between the theoretical values and unity (Neal *et al.*, 1994; Neal, 1996). No simple relationship occurs between H^+ and Al^{3+} or between either of these ions and the major cations and there is a great deal of scatter in the data. In a parallel study, using soil lysimeter data, similar incompatibilities were observed (Neal *et al.*, 1992d).

Thus, while there is a broad agreement between the cation concentrations and the sum of the anions, there is no proper compatibility with the cation exchange formulations used in most acidification models. The Plynlimon results are not exceptional because nearly identical results are found for an acidified moorland site in southern Norway (Neal, 1996) and for a Holm oak catchment in north-eastern Spain (Avila *et al.*, 1995). Further, previous work at Plynlimon indicates that aluminium release to drainage water can be associated with kinetic 'weathering'

type reactions involving proton consumption (Reynolds and Hughes, 1986; Reynolds *et al.*, 1989).

These findings, together with the evidence from long term trends of a decoupling of the base cations from hydrogen ion and aluminium concentrations (Dillon *et al.*, 1987; Driscoll *et al.*, 1989; Christophersen *et al.*, 1990a), cast doubt upon the value of the commonly used cation exchange equations (Neal *et al.*, 1997b).

Thus, the mobile anion theory, which is almost universally evoked in acidification models, seems irrelevant.

CHEMICAL REACTIONS OCCURRING DURING MIXING REACTIONS

Although emphasis has been placed on assessing the underlying chemical reactions that determine the chemistry of the stream-, soil- and ground-waters, it is clear that mixing reactions are important in all three water types. Within acidification research, one of the major assumptions is that, in all three zones, chemical equilibrium determines aluminium concentration based on aluminium hydroxide solubility (Neal, 1988a). One of the main chemical findings for aluminium within the Plynlimon catchments is that no such equilibrium exists (Neal, 1988b; Neal *et al.*, 1992d). In the stream, a combination of water mixing and aluminium precipitation reactions seems to occur: the dissolved inorganic aluminium is precipitated as aluminium hydroxide when the mixed waters are oversaturated with respect to this phase (Neal and Christophersen, 1989). However, there is considerable scatter in the mixing data and aluminium is complexed to different and erratic degrees with fluoride, organic matter and hydroxide (Neal, 1995). For the soil and groundwater areas, no clear patterns occur.

Discussion

GENERAL

The Plynlimon hydrochemical studies show a system that is highly heterogeneous with the chemical characteristics of surface-, soil- and ground-water chemistry varying over space and time and at different scales. For the longer term, of the order of tens of years, there are both systematic and random atmospheric inputs which affect stream water compositions. These inputs relate to both sea-salt and pollutant components. Potentially, these variations can affect the water quality and ecology of streams (e.g. chromium, Neal *et al.*, 1996) and yet no current atmospheric or catchment model has or could have predicted the Plynlimon water quality observations. On a more irregular basis, it seems that some environmental trigger has resulted in spasmodic nitrate releases to the streams which may influence patterns of behaviour for many years later. Such a phenomenon is of relevance to the growing concern of nitrogen critical loads and the associated intensive modelling activity presently being undertaken (Jenkins *et al.*, 1997; Reynolds, 1997; Cosby *et al.*, 1997). Work in this area is needed as climate variability is not taken into account. Such features of both regular and irregular change are not confined to the Plynlimon area but are observed world wide (cf. Christophersen *et al.*, 1990b; Likens and Bormann, 1995; Lange *et al.*, 1995; Manderscheid *et al.*, 1995).

In the shorter term (sub-weekly), the patterns of behaviour are much more regular for Plynlimon, at least as observed in the stream, owing to the dominance of hydrological controls.

With regard to spatial variability, clearly there are major constraints associated with erratic flow pathways and varying weathering rates both in the soil and groundwater areas. Because of the degree of complexity, it is difficult to identify the underlying chemical and hydrological processes at anything other than a descriptive level.

DETERMINATIVE HYDROLOGICAL AND CHEMICAL PROCESSES

The problem with understanding both the hydrological and chemical functioning of the Plynlimon catchments is an inability to measure the key properties at the scale that is needed to determine, quantitatively, the underlying interactive chemical, hydrological and biological processes. For example, the hydrochemical processes often involve non-linear equations that have been derived for homogeneous environments. In terms of hydrology, a start from first principles is not available because the simplifications generally used for describing flow through porous media cannot be applied to the shallow soils in upland catchments. For the chemical aspects, there is no adequate thermodynamic theory to partition the chemical transfers between the mobile and immobile soil water environments (Christophersen and Neal, 1990; Neal, 1996). Terms such as the classical mass action equations which apply in a homogeneous situation, no longer apply in a heterogeneous world: only the mass and charge balance terms remain strictly applicable. The work on testing the cation exchange models at Plynlimon highlights a missing or incorrectly posed process fundamental to acidification research and environmental management of acid sensitive ecosystems. Indeed, the heterogeneous features at localized parts of the catchment are damped out at the catchment outlet. This type of behaviour resembles that associated with a very active and developing area of scientific research called complexity theory. Here, one is concerned with how properties at the local scale determine global characteristics. Recent research has highlighted many areas of the environmental sciences where patterns at the macroscopic scale appear simple, but where immense complexity is observed at the microscopic level even though the determining mechanisms may well be described by simple rules (Cohen and Stewart, 1994). However, the simple emergent rules identified must be determined from field observa-

tions: theory explains only the broad reasons for the occurrence of a particular phenomenon.

DEFORESTATION

One of the clear findings of the Plynlimon experiment is that while tree harvesting does lead to a deterioration in stream water quality, the perturbations are relatively small. Indeed, it is not clear that any harm to stream water biology or resource results—for the Plynlimon area at least. The catchment-wide felling exercise at Plynlimon was undertaken more rapidly and more extensively than would normally occur in practice for the purposes of scientific research. Hence, the water quality changes would tend to be even smaller with the standard and more benign methods of harvesting. However, this does not mean that forestry practice will not result in a significant long-term deterioration in stream water quality because a second generation of forest might cause a more severe form of acidification (Jenkins *et al.*, 1990; Ferrier *et al.*, 1993). The factor central to determining the degree of acidification is the source of base cations that might enter the growing biomass. If base cations come from weathering sources, then acidification need not occur: indeed, with base cation cycling acidification could be partially reversed. However, if, as currently modelled, the cations come from the exchange complex in the soil, then acute acidification could occur. At present, it is unclear where the balance lies between these two sources. It is imperative that this lack of knowledge is rectified in deriving future planting policies. Furthermore, it is unclear as to the extent to which the trees can scavenge base cations as dust from the atmosphere.

THE INTERPLAY BETWEEN MEASUREMENT AND MODELLING APPROACHES

Current environmental modelling and critical load assessment centres on long standing concepts and, in some cases, on models that were formulated in the 1980s. It is unclear how reliable the models are in predictive mode given that, in almost every aspect, the Plynlimon findings differ from the assumptions made; there is a mismatch over (a) heterogeneity, (b) cation exchange formulations (c) aluminium solubility controls and (d) the foundations of the mobile anion concept. Furthermore, the chemical tracing experiments cast doubt on the underlying concepts of how water moves through catchments and how the hydrology should be represented within a modelling framework. This does not mean that the existing environmental management approaches will change given existing social and political pressures. Indeed, the individual scientist and the scientific peer group structure is affected by these social pressures (Kühn, 1962). The modern pressures and interlinkages within the environmental sciences and elsewhere, reflects what in philosophical terms is known across many disciplines as the 'postmodern condition' (Lyotard, 1994; Horrocks and Jevtic, 1996; Ward, 1997). However, in the light of Plynlimon findings it must be concluded that little trust can be placed in the predictive capacity of the current hydrochemical and environmental impact models associated with acidic deposition. Their use in determining environmental management policies may well be overemphasised, misplaced and counterproductive.

Despite this, models such as Birkenes (Christophersen *et al.*, 1982, 1984), MAGIC (Cosby *et al.*, 1985a,b), ILWAS (Gherini *et al.*, 1985) and PROFILE and SAFE (Sverdrup, 1996) have been of great value in the development of acid deposition research. For example, within a modelling framework, all the assumptions made are clearly stated and open to scientific scrutiny: this is not always the case with descriptive approaches to catchment science. Furthermore, the models can only use existing equations for the chemical processes operative in the field and more refined and representative formulations have not been produced which describes the features reported in this paper. The models serve an extremely valuable purpose of providing learning tools for examining the dynamics of water quality change both within the framework of hydrological events and of long term changes in catchment stores and evolving endmember compositions. For example, they allow an indication of how climate change (Avila *et al.*, 1996), forestry practices (Neal *et al.*, 1986, 1995; Jenkins *et al.*, 1990; Ferrier *et al.*, 1993; Forti *et al.*, 1995) and certain key areas of catchment (Hooper *et al.*, 1992; Forti *et al.*, 1996) might critically control the acidity of streams and influence the impacts of changing acidic deposition. Indeed, when model results conflict with observations (e.g. as with the Birkenes modelling example given above) then new insights may be gained into how catchments function; this is the basic principle of the scientific approach (Popper, 1994). The interplay between models and measurements provides an important example of how environmental science has progressed within acidification research (Christophersen and Neal, 1990; Cosby *et al.*, 1996).

Within modelling, the chemical signals at the stream outlet are relatively easy to simulate and there are often problems of over-parameterization and lack of identifiability of the determinative processes (Christophersen *et al.*, 1993; Hauhs *et al.*, 1996). Thus, data fitting well within a model is a prerequisite not an endorsement of its validity. In predictive mode, the main objective of environmental models must be to describe change and not to focus on the steady state case. Perhaps the greatest hindrance to assessing future environmental impacts is the lack of 'user friendly' easily-modifiable simulation models presently available. This shortfall is important for environmental research as there is a need to examine different 'what if' hypotheses through 'different pairs of eyes'. One future goal of modelling endeavours should be the development of a Functional Unit Network approach to modelling where soil compartments are defined in relation to user-stipulated chemical, biological and hydrological processes

and the compartments are embedded within a network of interlinked units. This approach, the inverse of a neural network design, could facilitate the foundations of a way of incorporating heterogeneous behaviour within a modelling structure: the question of parameter identifiability becomes of second order importance compared with examining the range of scenarios produced by the various modelling structures. This development is needed to move towards assessing structural rather than parameter uncertainty within models within the theme of emergent properties. Put another way, the only thing 'one can know of uncertainty' is that 'one is uncertain'. By exploring different structural models, some feel for the range of potential environmental impacts will be gained that will warrant further study. This contrasts with current analysis based on parameter uncertainty which starts off with the assumptions that a model is correct and that a distribution of parameter uncertainty is known. An assessment of parameter uncertainty provides no information of any use for deciding the overall predictive errors.

Conclusion

There is a developing belief among environmental managers, funding agencies and policy makers that environmental scientists now understand the mechanisms operating within ecosystems well enough for environmental impacts such as acid deposition to be assessed with the necessary degree of certainty. However, the Plynlimon study and elsewhere (Hauhs *et al.*, 1996) show that the internal hydrobiogeochemical functioning of a catchment is hard or maybe even impossible to unravel at a detailed process understanding level due to the complexity and interactive nature of the processes involved. Indeed, the more detailed the examination of the complexity of catchment responses, as at Plynlimon, the more complex the system seems to be and the greater the number of questions and uncertainties that arise. Despite this, at a broad level, the Plynlimon catchment acts in a simple mode and routine observations such as alkalinity measurements, when coupled to 'naive' approaches such as endmember mixing analysis, point clearly towards process understanding. Indeed, such a broad approach may well lead to more focused schemes for reassessing weathering rates and reversing acidification (Neal *et al.*, 1997c).

Many catchment experiments have been established worldwide over the last forty years to consider background, perturbed and changing environmental systems. Catchments provide a focal point for environmental studies and a test bed for environmental modelling. They provide evidence of how environmental systems function and evolve in an ever changing world. The hydrochemical responses at Plynlimon and elsewhere exemplify the need for data on the decadal to centennial scale for a wide range of environmental and chemical determinands if only for a few selected catchments for which associated long term hydrological data are available. Catchment research must be broadened to integrate hydrological, biological and hydrochemical research in a more holistic manner to achieve the best and most efficient thrust for the research needed in future years. May long-term catchment research survive and long flourish.

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